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MATERIALS TECHNOLOGY DEPARTMENT
Culver City, California

Literature Review of the Compatibility of Commercial Materials with Ethylene Oxide-Freon 12 Sterilant Gas Mixture

by

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1 of 7

ABSTRACT

The literature published after January 1962 was reviewed to uncover information on the compatibility of commerical materials with an ethylene oxide-Freon 12 gas mixture.

Ethylene oxide is capable of producing changes in material properties by reacting directly with base material or with impurities included during the manufacturing process. Because the reaction process is diffusion dependent, permeability of materials to the gas is an important factor. Freon 12 has solvent properties and tends to produce swelling in some elastomers. The majority of materials appearing on the first list should undergo relatively small change when exposed to sterilant gas at room temperature.

INTRODUCTION

A necessary phase of the sterilization regime used to destroy or diminish microorganism population on spacecraft is a sterilant gas exposure cycle. Materials damage, incurred through these procedures, can cause total failure or performance degradation of components in which the vulnerable materials are used. The compatibility of component materials with the 12% ethylene oxide 88% Freon 12 gas mixture must be determined to establish the reliability of spacecraft systems after sterilization procedures.

To augment information from an experimental compatibility study, a literature search was implemented to uncover published information on the behavior of the sterilant gas mixture with commercial materials. Materials of primary interest in this survey are those appearing on the first list submitted by JPL for test. Because of a similar search made in 1962 [3] references appearing before January 1962 were not reviewed.

The recent literature provided very little compatibility data. The major portion of the information given in this report is taken from literature published prior to 1962 and from the results of an experimental study performed as part of the Surveyor Sterilization Program.

In addition to reviewing the formal literature, letters were written to prime suppliers of ethylene oxide requesting handling manuals, materials compatibility lists, and general information. Where applicable, data from the manufacturer is included in this report. This report confines itself to the compatibility of materials appearing on the first JPL list. Additional general information on the chemistry of ethylene oxide, abstracted from the recent literature can be found in Reference 11.

LITERATURE REVIEW

Ethylene Oxide - A mixture of 12% ethylene oxide 88% Freon 12 is an effective vapor phase sterilant. The mechanism by which ethylene oxide kills microorganisms has been linked to chemical activity as an alkylating agent [1]. Ethylene oxide replaces labile hydrogen atoms present in carboxyl, amino, sulfhydryl and hydoxyl groups with hydoxyethyl ($-CH_2CH_2OH$) groups, thereby blocking many reactive groups participating is essential metabolic reactions.

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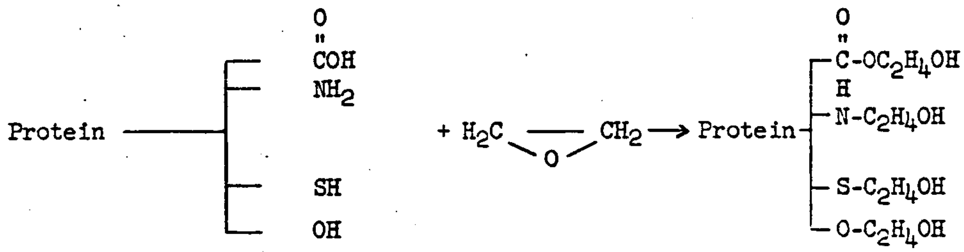
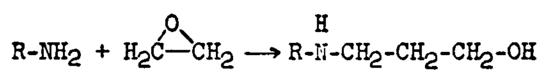
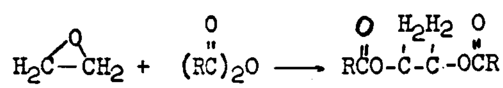
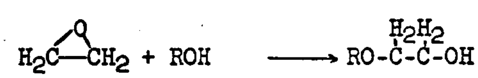


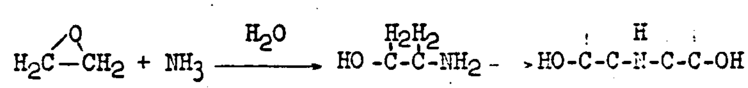
The ability of ethylene oxide to react with labile hydrogen makes it a potententially hazardous material for prolonged contact with commercial polymers such as epoxys. Amines, commonly used as curring agents in epoxy systems, are vulnerable to attack.

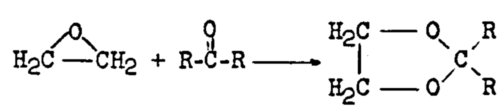


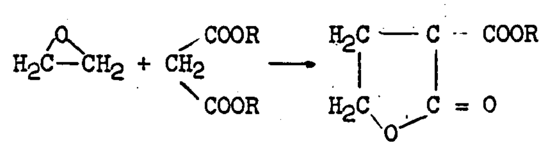
Ethylene oxide can participate in a number of reactions with compounds commonly found in commercial materials such as curing agents, fillers, plasticizers, and residual processing solvents[7 & 8]. Other materials such as metal and metallic oxides serve to catalyze the polymerization of ETO.

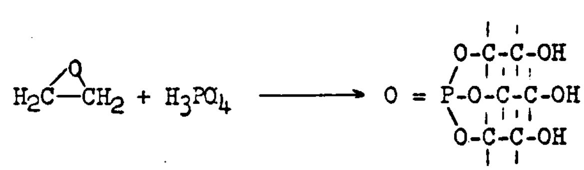
Acid Anhydrides 

Alcohols-Phenols 

Ammonia 

Ketones 

Malonates 

Phosphoric Acid 

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Polymerization (Metal Oxide Catalyzed)	$n\ H_2C{-}CH_2\ (\text{O})$	$\longrightarrow$ -C-CO-(C-C-O-)$_{n-2}$-C-C-O-
Silicon Tetrachloride	$H_2C{-}CH_2\ (\text{O})$ $+ SiCl_4$	$\longrightarrow Cl_3SiOC{-}C{-}Cl \rightarrow Cl_2Si(OC{-}C{-}Cl)_2$
Thiols	$H_2C{-}CH_2\ (\text{O})$ + RSH	$\longrightarrow$ HO-C-C-SR
Water	$H_2C{-}CH_2\ (\text{O})$ + H_2O	$\longrightarrow$ HO-C-C-OH $\longrightarrow$ OH-C-C-O-C-C-OH

Reaction with ethylene oxide can greatly modify the physical characteristics of a material. The overall change in properties of a material which contains reactive constituents or is itself reactive, is dependent on several factors.

1. The amount of reactant material present.
2. The permeability of the material to ethylene oxide.

Materials display a marked degree of difference in permeability to ethylene oxide[6]. The measurements by Waack[5] on commercial plastic sheets show the following relative permeabilities for packaging materials:

Cellophane 300 PT62	= 0.00
Polyvinyl alcohol	= 0.00
Polyester polyethylene terephthalate	= 0.00
Polyvinylidene chloride	= 0.1
Polyethylene	= 0.35
Polyvinyl chloride-nitrile rubber blend	= 1.0
Cellulose acetate - rigid	= 1.0
Cellulose acetate - plasticized	= 2.4
Polyvinyl chloride	= 2.0
Ethyl hydroxy ethyl cellulose	= 3.4
Ethyl cellulose	= 3.9

It is interesting to note that the addition of a plasticizer to cellulose acetate increases the permeability by a factor of 2.4, indicating that its behavior with ethylene oxide is not so much influenced by the material as by the additive.

Permeability is affected by a number of factors. Amorphous polymers have higher permeabilities than crystalline polymers. Crystallinity alone, however, does not determine gas transmission rate, molecular symmetry and cohesive energy densities are also influencing factors. Materials such as polyvinylidene chloride, which have a highly symmetrical molecular structure and high cohesive energy density display low permeabilities. Poor symmetry interferes with molecular packing resulting in an open structure through which gas molecules can pass.

Freon 12 - Freon 12 ($C\ Cl_2\ F_2$), used as a diluent in the sterilant gas mixture, does not react chemically with materials appearing on the first JPL list at room temperature. It does have solvent properties [9] however and a small amount of swelling or crazing may be experienced with some materials, especially after extended exposure at 104°F. Elastomers experience pronounced swelling after prolonged contact with liquid Freon 12. In a series of exposures performed by duPont [10], Viton A showed 10% linear swell and Viton B 9%. Other materials such as Neoprene W and polyvinyl alcohol showed shrinkage, probably due to leaching of plasticizers by Freon solvent action. The presence of two fluorine atoms on the Freon 12 molecule contribute to its high stability. Neither the materials tested nor the test conditions should decompose the Freon, therefore reactive decomposition products are not expected to be present for reaction with materials being tested.

Materials Compatibility - The first list of materials received from JPL is reproduced in Table I. After each item is listed the suspected compatibility with the sterilant gas mixture based on experimental data from reference 2. In some instances insufficient information is available to form an opinion on compatibility. These materials are denoted by N. I. in the table. It should be emphasized that information given in Table I is a rough estimation of compatibility based on the behavior of similar materials or families of materials.

Table I - Compatibility of Materials with 12% Ethylene Oxide 88% Freon 12 Gas Mixture

Product (Commercial Designation)	Material Type	Suspected Compatibility (Degree of Properties Change)
AMS 3303/60	Silicone	SC
Epon 828/Z	Epoxy	SC
H-Film	Polyimide	NI
Laminate MIL-F-1349,FL-GE	.062C	NI
Laminate MIL-P-21466	Epoxy	MC
LS-53/70	Fluorosilicone	NC
Micarta H-2497	Epoxy-Fiberglass	NC
PR 1930-1/2	Silicone	NI
Pyre-ML RK-692	Polyimide	NI
RTV 11	Silicone	SC
RTV 60	Silicone	SC
RTV 108	Silicone	SC
RTV 140	Silicone	SC
RTV 615	Silicone	SC
RTV 881	Silicone	SC
RTV 891	Silicone	SC
Silastic 1410	Silicone	NI
Silastic PR 1930-2	Silicone	NI
Silgard 182	Silicone	SC
Stycast 1095/11	Epoxy	SC
Stycast 2651/11	Epoxy	SC
Tedlar 200, Type 30B	Polyvinyl Fluoride	SC
Viton B 60 & 95	Fluorocarbon	MC
XP-206 Fiberglass	Epoxy	NC
2-218-5417-7	Silicone	NI
4000-80	Silicone	NI
7000-80	Silicone	NI

NC = no change in properties
SC = small change
MC = moderate change
NI = insufficient information

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